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Emission and Absorption in the Infra-Red Spectrum of Mercury.

By RAYMOND C. DEARLE, M.A., University of Toronto.

(Communicated by Prof. J. C. McLennan, F.R.S. Received July 17, 1916.)

INTRODUCTION.

In a previous paper by McLennan and Dearle,* it was pointed out that bands had been found in the absorption spectrum of non-luminous mercury vapour at $\lambda = 1849$ Å.U., $\lambda = 2536{\cdot}72$ Å.U., and $\lambda = 2338$ A.U., but that nothing had been done up to the present in the way of investigating the infra-red region of this spectrum for characteristic absorption bands. In the same paper an account was given of some measurements made on the infra-red emission spectrum of the mercury arc for the purpose of establishing the wave-lengths and intensities of the lines in that region. The present paper deals first with some additional work on the relative intensities of these lines, and, secondly, with the absorption bands produced by passing white light through non-luminous mercury vapour.

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* McLennan and Dearle, 'Phil. Mag.,' vol. 30, p. 683 (1915).

THE DISTRIBUTION OF INTENSITY IN THE LINES OF THE MERCURY SPECTRUM.

In the paper by Prof. McLennan and myself (*loc. cit.*) on the infra-red spectrum of the mercury arc, it was shown that there was a disagreement between the values of the relative intensities of the lines 0·5461 μ and 1·014 μ, as given by Paschen and by us. According to the former, the line 1·014 μ is the strongest in the arc spectrum of mercury, while in our investigation the line 0·5461 μ was found to be somewhat the stronger. It was pointed out by Paschen[*] that, with low vapour-pressures, the intensities of the two lines were about equal, while an increase in vapour-pressure caused a relatively greater increase in the intensity of the line 1·014 μ. Küch and Retschinsky,[†] in their measurements on the temperature of the mercury arc, found that an increase in current caused an increase in temperature, but did not affect the vapour-pressure, whereas an increase in voltage caused an increase both in temperature and in vapour-pressure. In Paschen's paper no mention is made of any variation in the voltage, but only of variations in current, so that, from the information given, it is not clear whether there was actually any variation in the vapour-pressure in his lamp, or merely variations in the temperature.

In a later paper by Küch and Retschinsky[‡] it was stated that, with higher temperatures in the mercury arc, the lines of shorter wave-length were relatively stronger than with lower temperatures, but no measurements were made on the line 1·014 μ. As this is analogous to the temperature effect for black body radiation, it seemed possible that the distribution of intensity in the lines of the spectrum might follow the usual form of the radiation curve. This point was investigated by Pflüger[§] and later by Grebe[||] with the result that it was established that lines belonging to the same series have their relative intensities arranged along a curve which is convex to the wave-length axis, that is, a curve resembling the short-wave portion of an energy curve. It was also found that an increase in temperature caused a relatively greater increase in the intensities of the shorter wave-lengths than in those of the longer wave-lengths. These relations, however, did not hold within a single triplet, nor among the lines as a whole. All of the wave-lengths investigated lay within the region of the visible spectrum or in the ultra-violet, and no observations were made on the infra-red wave-lengths, that is, in the region where the maximum of an energy curve would be expected to appear.

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[*] F. Paschen, 'Ann. d. Phys.,' vo[illegible] (13), p. 559 (1908).

[†] R. Küch and T. Retschinsky, [illegible] n. d. Phys.,' vol. 22 (3), pp. 595, 602 (1907).

[‡] R. Küch and T. Retschinsky, 'Ann. d. Phys.,' vol. 22 (5), pp. 852, 866 (1907)

[§] A. Pflüger, 'Ann. d. Phys.,' vol. 26 (4), pp. 789–805 (1908).

[||] L. Grebe, 'Phys. Zeitschr.,' vol. 11, pp. 1121–1122 (1910).

The present investigation was undertaken to find (1) whether, in the infra-red region, the relative intensities of the lines in a given series are distributed along an energy curve; and (2) the effect of increased temperature and vapour-pressure on the relative intensities of the two lines 0·5461 μ and 1·014 μ, which do not belong to the same series.

EXPERIMENTAL ARRANGEMENT.

The arrangement of the apparatus was the same as that previously described in the paper by Prof. McLennan and myself, except that the light from the mercury arc, instead of being focussed on the spectrometer slit by concave mirror, passed directly through a quartz lens having a focal length 20 cm. For the determination of the intensities of the various lines as distinguished from the continuous radiation due to the heated quartz, the method was followed of drawing a cooling curve for the lamp after extinguishing the arc. Greater precision was given to these measurements by taking logarithms of the galvanometer deflections and plotting these against elapsed time. This gave straight lines which could be continued back

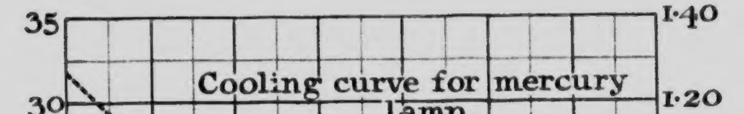

FIG. 1.

to zero time very accurately. An additional advantage of this method is that it was only necessary to take two readings with the galvanometer in order to obtain a complete curve. An example is given below, the curves being shown in fig. 1.

Elapsed time.	Deflection.	$\log_{10}$ deflection.
secs.	mins.	
8	12	1·0792
20	6	0·7782
33	3	0·4771
40	2	0·3010
55	1	0·0000

From the curve we get, for zero time, $\log_{10}$ deflection = 1·26 . . . hence, deflection due to radiation from the heated quartz = 18·2 mm.

RESULTS.

The lines chosen for the first part of the investigation were those belonging to the main series of single lines

$$n = (2{\cdot}5,\ \mathrm{S}) - (m,\ \mathrm{P}),^*$$

and the first three members of the series were used. These are given by

$$\begin{array}{ll} m = 2, & \lambda = 1{\cdot}014\mu, \\ \phantom{m = {}} 3, & \phantom{\lambda = {}} 1{\cdot}357\mu, \\ \phantom{m = {}} 4, & \phantom{\lambda = {}} 0{\cdot}6717\mu. \end{array}$$

The lamp was run with two different energy consumptions with the following results:—

Wave-length.	Intensity.	
	Energy = 230 watts.	Energy = 150 watts.
μ.		
1·357	6	6
1·014	20	14
0·6717	4	2

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* In the symbolic equation $\nu = (n,\ \mathrm{X}) - (m,\ \mathrm{X})$ the frequencies are given by $\nu = \frac{\mathrm{N}}{[n+\mathrm{X}+x(n,\ \mathrm{X})]^2} - \frac{\mathrm{N}}{[m+\mathrm{Y}+y(m,\ \mathrm{Y})]^2}$, where N is Rydberg's number, n has a fixed value either integral or one of the numbers 1·5, 2·5, 3·5, etc., and m has successive integral values, each one giving the frequency of a member of the series.

The curves for these results are shown in fig. 2. It should be noted that the intensities lie on curves which resemble the ordinary energy curves, in that they are steeper on the short-wave side, and the increase in energy is quite clearly relatively greater in the shorter wave-lengths. The lack of sufficient points on the curve prevented the necessary accuracy for determining whether the maximum intensity shifts to the shorter wave-lengths for increase in temperature. If this were so then the analogy to the energy curve would be complete. It is interesting to note that the distribution of energy is governed by the actual wave-lengths of the lines and not by the order in which they occur in the series; *i.e.*, although the first member of the series is $\lambda = 1{\cdot}014\,\mu$ and the second is $\lambda = 1{\cdot}357\,\mu$, the lines are distributed along the energy curve, not in this inverted order, but in the order of their wave-lengths.

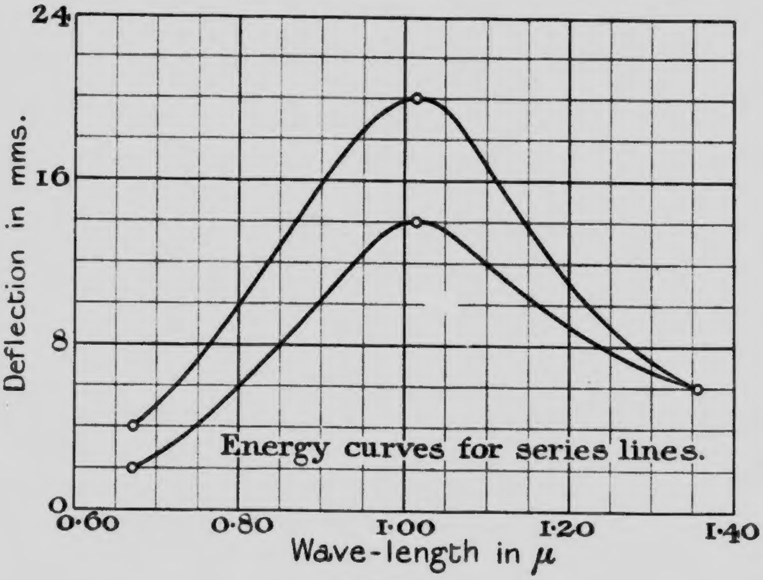

Fig. 2.

For the second part of the investigation the current in the lamp was kept constant at 3·2 ampères, and the voltage was varied so as to give an energy consumption in the lamp which ranged from 150 to 250 watts. For each of the applied voltages the intensity was measured on the line $1{\cdot}014\,\mu$ and on $0{\cdot}5461\,\mu$ by the method described above. The results are given in the Table below, the first column gives the energy consumption in watts, in the second column I_1 represents the intensity of the line $0{\cdot}5461\,\mu$, and I_2 in the third column gives the intensity of the line $1{\cdot}014\,\mu$. The fourth represents the ratio of the two intensities in each case.

Energy.	I_1.	I_2.	I_2/I_1.
watts.			
150	18	23	1·28
215	28	40	1·43
250	40	84	2·10

It will be noted from the last column that the relative intensity of the line 1·014 μ to that of the line 0·5461 μ increases regularly with increase in energy consumption, or in other words, with increase in vapour-pressure in the lamp. In all measurements with this lamp the line 1·014 μ always appeared to be the more intense.

II. Absorption by Mercury Vapour.

As far as the author has been able to ascertain there has been no work done by previous investigators on the selective absorption by non-luminous mercury vapour in the infra-red region. It was at first intended to pass the light from a mercury arc through a layer of the vapour and examine the emergent radiation to find whether any of the lines in the infra-red spectrum were extinguished. This method was abandoned, however, and the radiation from a Nernst glower was used instead of that from a mercury arc. The principal advantages in this were the greater steadiness in the radiation secured, and the fact that a continuous spectrum was produced in which absorption bands would take the form of depressions.

Apparatus.

The apparatus used for these measurements was similar to that used in the previous work. The spectrometer, thermopile, and galvanometer were unchanged, and the mercury lamp was replaced by the Nernst glower and the absorption cell. The latter is shown in section in fig. 3. It is made entirely of fused quartz, is about 6 cm. long and 3 cm. in diameter, with a small reservoir (C) for the mercury underneath. The ends were formed of two circular plates of clear fused quartz which transmitted the visible light with very little diffusion. A small tube (D) at the top served to connect the cell with an exhaust pump. The reservoir was first filled with clean dry mercury, which was boiled to eliminate all traces of water-vapour, and the cell was then exhausted to a pressure of a few millimetres of mercury and sealed off.

When in use the cell was heated by means of an electric current applied to the walls of the reservoir and tube, temperatures as high as 190° C. being used. In order to obtain uniform temperature and hence constant vapour density, the cell was placed in a box and packed in powdered magnesia. The

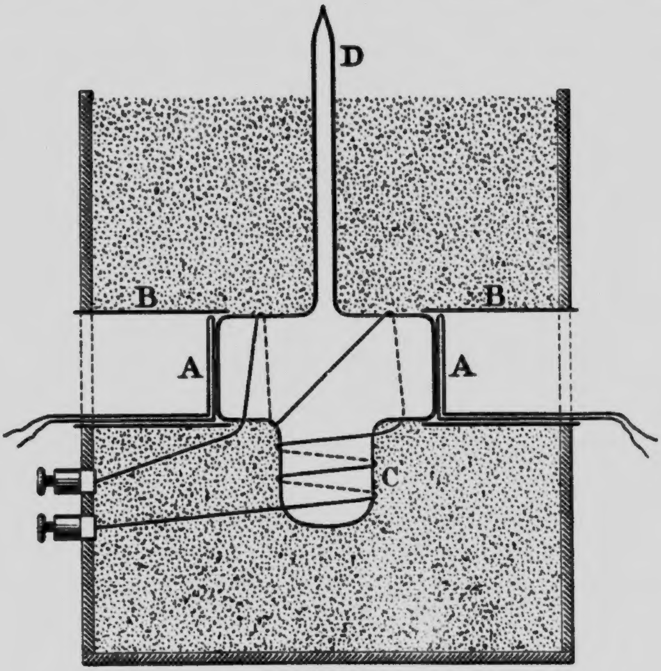

Fig. 3.

ends were kept clear for the transmission of the radiation by means of two brass tubes projecting it from the sides of the box, as shown at BB. It was found that on account of the radiation through these tubes, and the consequent lowering of the temperature at the ends of the cell, the mercury vapour immediately condensed on the end plates, thus cutting off the radiation very considerably. This difficulty was overcome by putting a single turn of wire against each plate from the outside (AA), and passing a current through these wires of sufficient strength to maintain the plates at a slightly higher temperature than the rest of the cell.

The light from the Nernst glower was first focussed on the slit of the spectrometer by means of a quartz lens; then the cell and its containing box was placed in such a position that the radiation from the Nernst glower had to pass through the cell before falling on the lens.

After all the readings had been taken, the absorption cell was replaced by a plate of clear fused quartz similar to those forming the ends of the cell. The intensity of the radiation was cut down by means of a diaphragm of Bristol board having a small hole cut in the centre, in order to make the galvanometer deflections comparable with those obtained when using the cell. Readings were taken over the spectrum with this arrangement so as to find out whether any of the observed absorption bands might be due to absorption by the quartz itself.

RESULTS.

The range of wave-lengths studied was from 1·00 μ to 1·20 μ, and this region was investigated very thoroughly. A great number of readings were necessary on each wave-length to obtain a satisfactory curve, and each set of readings was repeated over a period of several months. The necessity for this lies in the unsteadiness of the zero point in reading the galvanometer deflections, which was due to the combined effects of local magnetic disturbances on the galvanometer and stray air-currents on the thermopile. Despite these difficulties it was found that certain well-defined depressions occurred in every set of readings, while others were obtained which were not so well defined, sometimes appearing quite strong and at other times being scarcely detectable.

In the following Table are given all the wave-lengths at which absorption bands were observed and the characteristics of each one. The wave-lengths of the emission lines as recorded in our previous paper are given for purposes of comparison.

Emission.	Absorption.	Character of absorption.
μ.	μ.	
1·014	1·014	Strong, well-marked.
1·038	1·038	Very weak, doubtful.
1·067	1·065	Moderately strong.
1·090	1·089	Weak.
1·128	1·129	Strong.
1·170	1·160	Moderate.
1·205	1·20	Strong.

The temperatures used varied from 140° C. to 190° C., and an attempt was made to show that the strength of the weaker bands was dependent on the vapour-pressure within the absorption cell. But within the limits of these temperatures the results were entirely negative. Readings were then taken with the cell at the temperature of the room, about 20° C., and the resultant curves gave all the absorption bands as doubtful except those at 1·014 μ and 1·20 μ, absorption being quite distinct on both of these wave-lengths.

The final readings were taken, as described above, with a plate of clear quartz in the path of the radiation in place of the absorption cell. Readings were taken over the same range of wave-lengths and a smooth curve was obtained with no evidences of any characteristic absorption bands.

Some of the results are shown in the accompanying diagrams. Fig. 4 shows the band at 1·129 μ; figs. 5*a* and 5*b* show the band at 1·014 μ for temperatures 180° and 20° respectively; while figs. 6*a* and 6*b* represent the band at 1·20 μ for the same respective temperatures. It will be noted that neither fig. 5*a* nor fig. 5*b* shows any trace of the band at 1·038 μ.

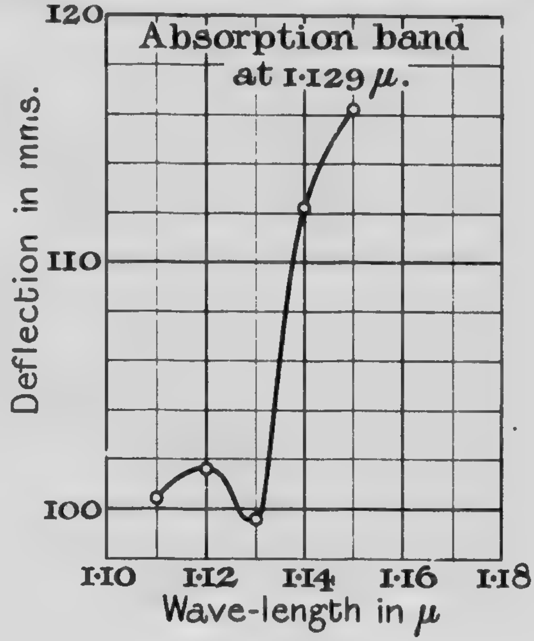

Fig. 4.

Discussion of Results.

A study of the list of absorption bands given above shows that at least some evidences of absorption were found on every wave-length for which there is an emission line in the spectrum of the mercury arc. The only anomalous result is the band at 1·160 μ instead of at 1·170 μ. That this is not an error in the readings is shown by the fact that the band appeared quite definitely at wave-length 1·160 μ in practically every set of readings. Three of the bands are given in the Table as being strong and well defined, namely, those at 1·014 μ, 1·129 μ, and 1·20 μ. If we take the corresponding emission lines we find that the line at 1·014 μ is the most intense in the whole mercury spectrum; the one at 1·128 μ ranks next in intensity to the line 1·014 μ in the infra-red portion of the spectrum; while the emission line at 1·205 μ is only very weak in intensity. We also find in regard to these lines that 1·014 μ is the first line of the main series of single lines

$n = (2{\cdot}5, \mathrm{S})-(m, \mathrm{P})$; while the line 1·205 μ is given by Paschen* as the first line of the combination series $n = (2, \mathrm{P})-(m, s)$ and also as the first line of a second combination series $n = (1{\cdot}5, s)-(m, \mathrm{P})$.

This is quite significant in view of the fact that the absorption bands at 1·014 μ and at 1·20 μ appeared when the temperature in the cell was as low as 20° C., that is, with very small vapour-pressure. It is hence quite justifiable to say that absorption takes place most readily on these two lines and this gives a greater theoretical importance to the series of which these are the first members. It is probable that the series $n = (1{\cdot}5, s)-(m, \mathrm{P})$ is the important one in connection with the line of longer wave-length on account of its close relationship to the series $n = (2{\cdot}5, \mathrm{S})-(m, \mathrm{P})$, of which 1·014 μ is the first member.

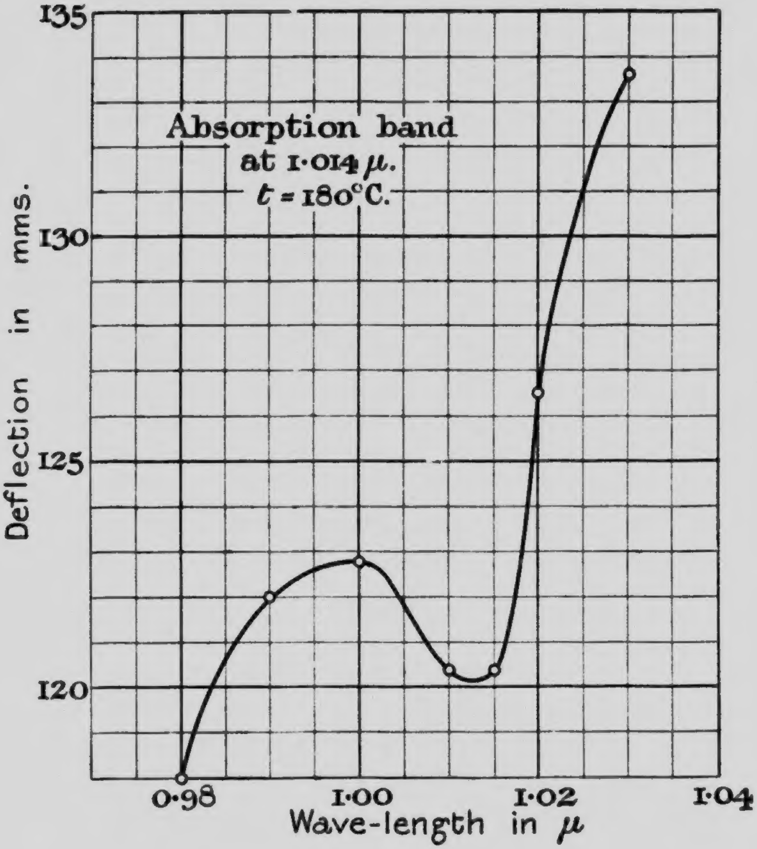

FIG. 5A.

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* F. Paschen, 'Ann. d. Phys.,' vol. 35, p. 869 (1911).

R. W. Wood[*] and McLennan and Edwards[†] have shown that there is absorption by non-luminous mercury vapour at wave-lengths 2536 Å.U., 2338 Å.U., and 1849 Å.U. Of these, the corresponding emission line at 2536 Å.U. is the first member of Paschen's combination series $n=(2, p_2)-(m, S)$; while the line at 1849 Å.U. is the first member of the principal single-line series $n = (1{\cdot}5, S)-(m, P)$. Thus we have four well marked frequencies associated with the mercury atom, two in the infra-red and two in the ultra-violet, each of which is the first member of a series in the spectrum of the mercury arc.

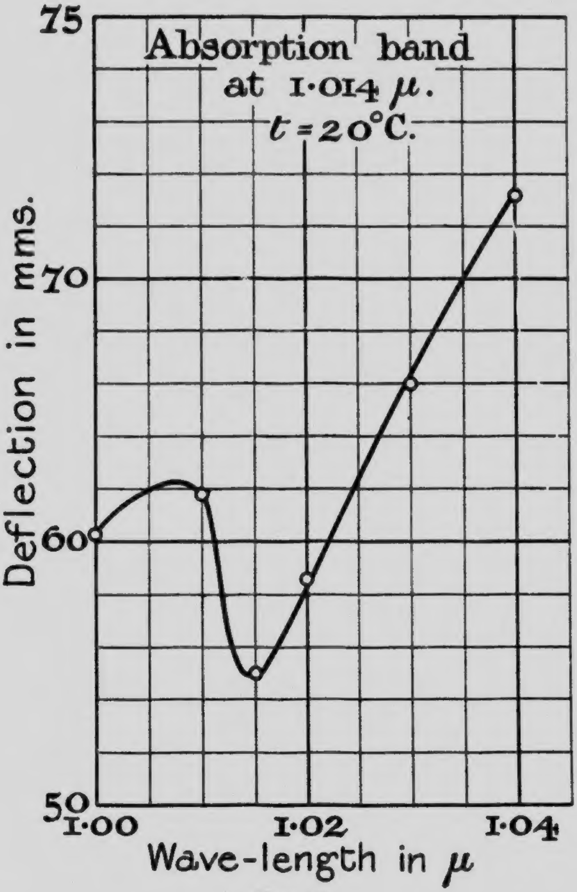

FIG. 5B.

The line at 2536 Å.U. is the one which appears in the single-line spectrum

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[*] R. W. Wood, 'Physical Optics,' p. 431.

[†] McLennan and Edwards, 'Proc. Roy. Soc., Canada,' 1915.

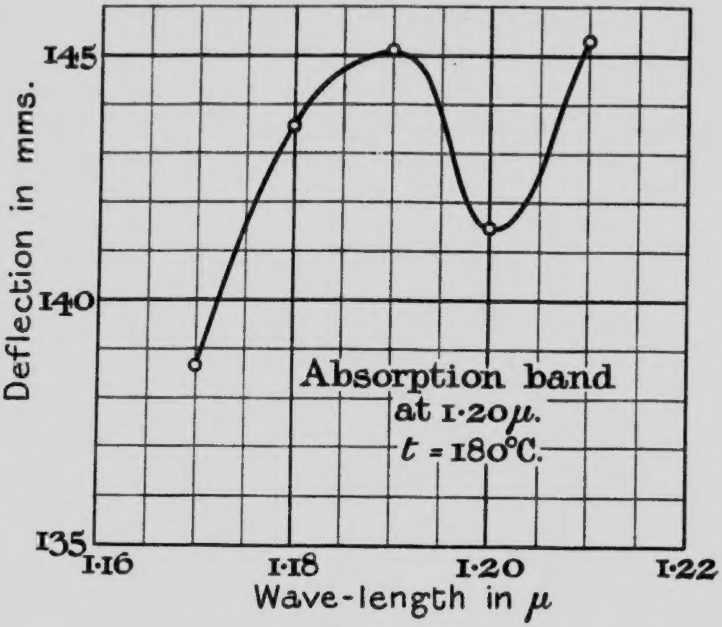

Fig. 6A.

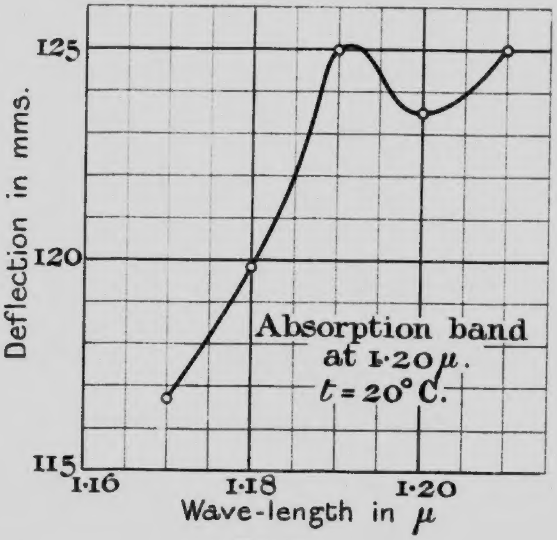

Fig. 6B.

of mercury, as given by Frank and Hertz* and by McLennan and Henderson.† It is possible that one of these infra-red lines may also appear in this spectrum, but it is difficult to see how its presence could be detected, as the intensity of the line 2536 Å.U. is so small as to require an exposure of at least one hour in order to produce an impression on a photographic plate. It has recently been shown by Prof. McLennan and Mr. A. Thomson that this same line is given out by mercury vapour in a Bunsen flame, and an attempt was made to see if the radiation of wave-length $\lambda = 1·014\,\mu$ could be detected as well from such a source. The experiments, however, failed to reveal any indication of the emission of such radiation.

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* Frank and Hertz, 'Verh. d. Deutsch. Phys. Ges.,' vol. 11, p. 512 (1914).

† McLennan and Henderson, 'Roy. Soc. Proc.,' vol. 91, p. 485 (1915).

SUMMARY OF RESULTS.

1. *Emission.*

1. It has been established that the relative intensities of the lines in an individual series lie along a curve analogous to an energy curve, not only in the region of short waves, but also in the long-wave region beyond the maximum of the energy curve.

2. The intensities of the series lines become relatively greater in the shorter wave-lengths with increase in temperature.

3. For the two lines, $1·014\,\mu$ and $0·5461\,\mu$, which do not belong to the same series, the intensity of the former becomes relatively greater for higher temperatures and increased vapour-pressures, although it is the line of longer wave-length.

2. *Absorption.*

1. Evidences of absorption have been found with each wave-length for which there is an emission line in the mercury spectrum between $1·00\,\mu$ and $1·20\,\mu$.

2. Strong absorption was obtained on wave-lengths $1·014\,\mu$, $1·129\,\mu$, and $1·20\,\mu$.

3. Absorption was obtained at wave-lengths $1·014\,\mu$ and $1·20\,\mu$, with very low vapour-pressure.

4. It has been shown that these two wave-lengths correspond to the first members of the series $\nu = (2·5, \mathrm{S})-(m, \mathrm{P})$, and $(1·5, s)-(m, \mathrm{P})$, respectively

In conclusion, the author wishes to acknowledge his indebtedness to Prof. J. C. McLennan for suggesting the investigation, and for his kind direction and helpful suggestions through its progress.

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